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(54) Abstract Title

Preparation of melamine flame-proofed flexible polyurethane foams

(57) Flameproofed flexible polyurethane foams are prepared by reacting organic and/or modified organic polyisocyanates (a) with a polyetherol mixture (b) and, if required, further compounds (c) having hydrogen atoms reactive toward isocyanates, in the presence of water and/or other blowing agents (d), catalysts (e) stabilizers (f), flameproofing agents (g) and, if required, further assistants and additives (h), by a process in which the polyetherol mixture (b) comprises

b1) at least one polyetherol which is at least difunctional and based on propylene oxide and/or butylene oxide and ethylene oxide, the ethylene oxide content being less than 25% by weight, based on the total amount of alkylene oxide used, has an OH number of from 20 to 80 mg KOH/g and contains more than 70% of primary OH groups and

b2) at least one polyetherol which is based on propylene oxide and/or butylene oxide and ethylene oxide, has an OH number of more than 30 mg KOH/g and contains less than 70% of primary OH groups, and melamine, if desired as a mixture with further flameproofing agents, is used as flameproofing agent (g).

The flameproofed flexible polyurethane foams prepared by this process can be used as upholstery for furniture and vehicle seats.

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Preparation of flameproofed flexible polyurethane foams

The preparation of polyurethane foams by reacting organic and/or
5 modified organic polyisocyanates or prepolymers with compounds
having a high functionality and at least two reactive hydrogen
atoms, for example polyoxyalkylene polyamines and/or preferably
organic polyhydroxy compounds, in particular polyetherols, having
molecular weights of from 300 to 6000, and, if required, chain
10 extenders and/or crosslinking agents having molecular weights of
up to about 400 in the presence of catalysts, blowing agents,
flameproofing agents, assistants and/or additives is known and
has been widely described. A comprehensive overview of the
preparation of polyurethane foams appears, for example, in
15 Kunststoff-Handbuch, Volume VII, "Polyurethane", 1st Edition
1966, edited by Dr. R. Vieweg and Dr. A. Höchtlen, and 2nd
Edition, 1983, and 3rd Edition, 1993, each edited by Dr. G.
Oertel (Carl Hanser Verlag, Munich).

20 For numerous applications, it is often necessary to provide
polyurethane foams with flameproofing agents in order to minimize
the fire risk of such materials. In addition to sufficiently well
known halogen-containing flameproofing agents, which are
undesirable in particular for ecological reasons, melamine is a
25 very suitable and widely used flameproofing agent, particularly
in flexible foams. It is possible in many cases to achieve
flameproofing according to Crib-V standard.

Thus, in EP-A-0422797, a combination of melamine and polyurea
30 polyols is used for flameproofing in flexible foam. In
EP-A-0439719, inter alia, cyanuric acid derivatives are used for
flameproofing in addition to melamine. EP-A-0642543 refers to the
fact that, particularly with the use of melamine, there is
considerable softening of the foam, which is to be considered
35 disadvantageous for our intended uses. EP-A-482 507 describes, as
a flameproofing agent, a combination of expanded graphite,
melamine and ammonium polyphosphate. Here, the expanded graphite
preferably serves for preventing melamine from settling out.
Expanded graphite having a particle size of < 0.5 mm is therefore
40 proposed as being particularly preferred. With such a small
particle size, however, the expansion effect on which the
flame-retardant action of the expanded graphite is based is too
small.

45 In CA 2203730, an attempt is made to realize the required
flameproofing in flexible foams by introducing PVC paste into the
PUR mixture. Considerably amounts are required. WO-A-9823678

- describes the use of melamine and red phosphorus, the foams in this case being rigid integral foams of relatively high density. Both flameproofing agents are said to have an improved effect, flameproofing in a relatively high density range generally being easier to realize. In the preparation of flame-retardant PUR foams, DE-A-3732238 refers to impregnation of the foam with polychloroprene and aluminum hydroxide, which is an expensive process. The use of halogenated phosphonate esters based on dibromoneopentylglycol is said, according to DE-A-2166942, to lead to flame-retardant PUR foams. EP-A-835905 describes the preparation of melamine dispersions which are stable to settling. According to said publication, flameproofing can be realized up to the Crib V level.
- 15 US-A-5177118 describes specific prepolymers having an NCO content of from 2 to 15% by weight, which is said to have advantageous effects on the flameproofing.
- According to US 5506278, PHD polyols in combination with melamine are said to give flameproofed flexible PUR foams. Similarly, DE-A-3530519 mentions a flameproofed foam which, in addition to melamine as a base flameproofing agent, contains in particular a polymer polyol.
- 25 Expanded graphite is frequently employed for obtaining a highly flameproofed foam. EP-A-337228 describes polyurethane foams whose polyol components are polyester alcohols and which contain, as a flameproofing agent, a mixture of expanded graphite and ammonium phosphate, calcium carbonate, calcium cyanamide or hydrated aluminum oxide. The polyurethanes described therein, however, have pure fire behavior. EP-A-358 985 discloses polyurethanes which, in addition to expanded graphite, also contain ammonium polyphosphate, calcium cyanamide, hydrated aluminum oxide or calcium carbonate as a flameproofing agent and into whose preparation polyurea-polyol dispersions were used. EP-A-414 868 describes polyurethanes which contain, as a flameproofing agent, expanded graphite which has a particle size of from 0.3 to 1 mm and is incorporated into the cell walls of the polyurethane foam.
- 35
- 40 The inventions mentioned in the prior art entirely permit the preparation of flameproofed flexible polyurethane foams which in particular pass the Crib V test, this class of substance still having considerable potential for improvement with regard to complying with the requirements of the Crib VII test and the
- 45 processibility of such formulations.

It is an object of the present invention to provide a process for the preparation of flameproofed flexible polyurethane foams (Crib VII), in which, owing to the polyol combination used, in particular the decomposition behavior of the foams in the course of the fire is advantageously altered and hence the effect of the flameproofing agents is improved.

We have found, surprisingly, that this object is achieved if a specific polyol combination, consisting of

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b1) at least one polyetherol which is at least difunctional and based on propylene oxide and/or butylene oxide and ethylene oxide, the ethylene oxide content being less than 25% by weight, based on the total amount of alkylene oxide used, has an OH number of from 20 to 80 mg KOH/g and contains more than 70% of primary OH groups and

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b2) at least one polyetherol which is based on propylene oxide and/or butylene oxide and ethylene oxide, has an OH number of more than 30 mg KOH/g and containing less than 70% of primary OH groups,

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is used in association with melamine and further flameproofing agents.

25

The present invention accordingly relates to a process for the preparation of flameproofed flexible polyurethane foams by reacting organic and/or modified organic polyisocyanates (a) with a polyetherol mixture (b) and, if required, further compounds (c) having hydrogen atoms reactive toward isocyanates, in the presence of water and/or other blowing agents (d), catalysts (e), stabilizers (f), flameproofing agents (g) and, if required, further assistants and additives (h), wherein the polyetherol mixture (b) consists of

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b1) at least one polyetherol which is at least difunctional and based on propylene oxide and/or butylene oxide and ethylene oxide, the ethylene oxide content being less than 25% by weight, based on the total amount of alkylene oxide used, has an OH number of from 20 to 80 mg KOH/g and contains more than 70% of primary OH groups and

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b2) at least one polyetherol which is based on propylene oxide and/or butylene oxide and ethylene oxide, has an OH number of more than 30 mg KOH/g and contains less than 70% of primary OH groups,

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and melamine, if desired as a mixture with further flameproofing agents, is used as flameproofing agents (g).

The present invention furthermore relates to the flameproofed
5 flexible polyurethane foams prepared by this process and to their use as upholstery for furniture and vehicle seats.

In our investigations, we surprisingly found that, by using the novel combination of the polyols (b), the fire behavior of
10 flexible polyurethane foams can be influenced in such a way that the Crib-VII test is passed. Surprisingly, by means of the modified flexible phase, resulting from the novel polyol mixture, it was evidently possible to achieve a reduction in the phase transition of the decomposition products into the gas phase.

15 Regarding the components used according to the invention in the polyol mixture, the following may be stated:

Component (b1) consists of at least one polyetherol which is at
20 least difunctional and based on propylene oxide and/or butylene oxide and ethylene oxide, the ethylene oxide content being less than 25% by weight, based on the total amount of alkylene oxide used. The OH number of these polyetherols is from 20 to 80 mg KOH/g. They contain more than 70% of primary OH groups.

25 For example, the following are suitable as (b1): polyetherols based on glycerol, trimethylolpropane or sorbitol as an initiator. Owing to the terminal ethylene oxide block, they have predominantly primary OH groups. Polyetherols with glycerol or
30 trimethylolpropane, particularly preferably with glycerol, as an initiator are preferably used.

Component (b2) consists of at least one polyetherol which is based on propylene oxide and/or butylene oxide and ethylene
35 oxide, has an OH number greater than 30 mg KOH/g and contains less than 70% of primary OH groups.

For example, the following are suitable for this purpose: polyetherols with water, propylene glycol or glycerol as an
40 initiator. Polyols having an OH number of from 50 to 80 mg KOH/g are preferably used.

The weight ratio of component (b1) to component (b2) is advantageously more than 0.3, preferably more than 1.0.

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Said polyetherols are prepared by known processes, as described, for example, further below.

The novel flameproofed flexible polyurethane foams are prepared
 5 by reacting organic and/or modified organic polyisocyanates (a)
 with the polyetherol mixture (b) described above and, if
 required, further compounds (c) having hydrogen atoms reactive
 toward isocyanates, in the presence of water and/or other blowing
 agents (d), catalysts (e), stabilizers (f), flameproofing agents
 10 (g) and, if required, further assistants and additives (h).

The following may be stated specifically regarding the further
 starting components which may be used:

15 Suitable organic polyisocyanates (a) for the preparation of the
 novel polyurethanes of the aliphatic, cycloaliphatic, araliphatic
 and preferably aromatic polyfunctional isocyanates known per se.

Specific examples are alkylene diisocyanates having 4 to 12
 20 carbon atoms in the alkylene radical, such as dodecane
 1,12-diisocyanate, 2-ethyltetramethylene 1,4-diisocyanate,
 2-methylpentamethylene 1,5-diisocyanate, tetramethylene
 1,4-diisocyanate and preferably hexamethylene 1,6-diisocyanate;
 cycloaliphatic diisocyanates, such as cyclohexane 1,3- and
 25 1,4-diisocyanate and any desired mixtures of these isomers,
 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane
 (IPDI), hexahydrotolylene 2,4- and 2,6-diisocyanate and the
 corresponding isomer mixtures, dicyclohexylmethane 4,4'-, 2,2'-
 and 2,4'-diisocyanate and the corresponding isomer mixtures, and
 30 preferably aromatic di- and polyisocyanates, e.g. tolylene 2,4-
 and 2,6-diisocyanate and the corresponding isomer mixtures,
 diphenylmethane 4,4'-, 2,4'- and 2,2'-diisocyanate and the
 corresponding isomer mixtures, mixtures of diphenylmethane 4,4'-
 and 2,2'-diisocyanates, polyphenylpolymethylene polyisocyanates,
 35 mixtures of diphenylmethane 4,4'-, 2,4'- and 2,2'-diisocyanates
 and polyphenylpolymethylene polyisocyanates (crude MDI) and
 mixtures of crude MDI and tolylene diisocyanates. The organic di-
 and polyisocyanate may be used individually or in the form of
 their mixtures. Tolylene diisocyanate, mixtures of
 40 diphenylmethane diisocyanate isomers, mixtures of diphenylmethane
 diisocyanate and crude MDI or tolylene diisocyanate with
 diphenylmethane diisocyanate and/or crude MDI are preferably
 used. Mixtures of diphenylmethane diisocyanate isomers with at
 least 10% by weight of diphenylmethane 2,4'-diisocyanate are
 45 particularly preferably used.

Frequently, modified polyfunctional isocyanates, i.e. products which are obtained by chemical reaction of organic di- and/or polyisocyanates, are also used. Examples are di- and/or polyisocyanates containing ester, urea, biuret, allophanate, carbodiimide, isocyanurate, uretdione and/or urethane groups. Specific examples are reaction products of organic, preferably aromatic, polyisocyanates containing urethane groups and having NCO contents of from 43 to 15, preferably from 31 to 21, % by weight, based on the total weight, for example with low molecular weight diols, triols, dialkylene glycols, trialkylene glycols or polyoxyalkylene glycols having molecular weights of up to 6000, in particular having molecular weights of up to 1500, modified diphenylmethane 4,4'-diisocyanate, modified diphenylmethane 4,4'- and 2,4'-diisocyanate mixtures or modified crude MDI or tolylene 2,4- or 2,6-diisocyanate. The di- or polyoxyalkylene glycols may be used individually or as mixtures, examples being diethylene glycol, dipropylene glycol, polyoxyethylene, polyoxypropylene and polyoxypropylenepolyoxyethylene glycols, -triols and/or -tetrols. NCO-containing prepolymers having NCO contents of from 25 to 3.5, preferably from 21 to 14, % by weight, based on the total weight, prepared from the polyester polyols and/or preferably polyetherpolyols described below and diphenylmethane 4,4'-diisocyanate, mixtures of diphenylmethane 2,4'- and 4,4'-diisocyanate, tolylene 2,4- and/or 2,6-diisocyanates or crude MDI, are also suitable. Furthermore, liquid polyisocyanates containing carbodiimide groups and/or isocyanurate rings and having NCO contents of from 43 to 15, preferably from 31 to 21, % by weight, based on the total weight, for example based on diphenylmethane 4,4'-, 2,4'- and/or 2,2'-diisocyanate and/or tolylene 2,4- and/or 2,6-diisocyanate, have proven useful. The modified polyisocyanates may be mixed with one another or with unmodified organic polyisocyanates, e.g. diphenylmethane 2,4'-diisocyanate, diphenylmethane 4,4'-diisocyanate, crude MDI, tolylene 2,4-diisocyanate and/or tolylene 2,6-diisocyanate.

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Modified organic polyisocyanates which have proven particularly useful are NCO-containing prepolymers which are advantageously formed from the reaction of the isocyanates (a) with the polyetherols (b) and, if required, compounds of components (c) and/or (d).

45 added.

In addition to the polyetherol mixture (b) described above and used according to the invention, further compounds (c) having hydrogen atoms reactive toward isocyanates are, if required,

Compounds having at least two reactive hydrogen atoms are primarily suitable for this purpose. Those having a functionality of from 2 to 8, preferably from 2 to 3, and an average molecular weight of from 300 to 8000, preferably from 300 to 5000, are expediently used.

Polyols having a functionality of from 2 to 8, preferably from 2 to 3, and an average molecular weight of from 300 to 8000, preferably from 300 to 5000, are expediently used. The hydroxyl number of the polyhydroxy compounds is as a rule from 20 to 800, preferably from 20 to 100.

The polyether polyols used in the components (b) and (c) are prepared by known processes, for example by anionic polymerization with alkali metal hydroxides, e.g. sodium hydroxide or potassium hydroxide, or alkali metal alcoholates, e.g. sodium methylate, sodium ethylate or potassium ethylate or potassium isopropylate, as catalysts and with the addition of at least one initiator which contains from 2 to 8, preferably from 2 to 3, reactive hydrogen atoms in bound form per molecule, or by cationic polymerization with Lewis acids, such as antimony pentachloride, boron fluoride etherate, etc., or bleaching earths as catalysts, from one or more alkylene oxides having 2 to 4 carbon atoms in the alkylene radical. For specific intended uses, monofunctional initiators may also be incorporated into the polyether structure.

Suitable alkylene oxides are, for example, tetrahydrofuran, 1,3-propylene oxide, 1,2- and 2,3-butylene oxide, styrene oxide and preferably ethylene oxide and 1,2-propylene oxide. The alkylene oxides may be used individually, alternately in succession or as mixtures.

Examples of suitable initiator molecules are water, organic dicarboxylic acids, such as succinic acid, adipic acid, phthalic acid, terephthalic acid, aliphatic and aromatic, unsubstituted or N-monoalkyl- or N,N- and N,N'-dialkyl-substituted diamines having 1 to 4 carbon atoms in the alkyl radical, such as unsubstituted or monoalkyl- or dialkyl-substituted ethylenediamine, diethylenetriamine, triethylenetetramine, 1,3-propylenediamine, 1,3- and 1,4-butylenediamine, 1,2-, 1,3-, 1,4-, 1,5- and 1,6-hexamethylenediamine, phenylenediamine, 2,3-, 2,4- and 2,6-tolylenediamine and 4,4', 2,4'- and 2,2'-diaminodiphenylmethane. Other suitable initiator molecules are alkanolamines, e.g. ethanolamine, N-methyl- and N-ethylethanolamine, dialkanolamines, e.g. diethanolamine, N-methyl- and N-ethyldiethanolamine, and trialkanolamines, e.g.

triethanolamine, and ammonia. Polyhydric, particularly dihydric and/or trihydric, alcohols, such as ethanediol, 1,2- and 2,3-propanediol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane and
 5 pentaerythritol, are preferably used.

The polyetherpolyols, preferably polyoxypropylene- and polyoxypropylenepolyoxyethylenepolyols, have a functionality of, preferably, from 2 to 8, in particular from 2 to 3, and molecular
 10 weights of from 300 to 8000, preferably from 300 to 6000, in particular from 1000 to 5000, and suitable polyoxytetramethylene glycols have a molecular weight of up to about 3500.

Other suitable polyetherpolyols are polymer-modified
 15 polyetherpolyols, preferably graft polyetherpolyols, in particular those based on styrene and/or on acrylonitrile, which are prepared by in situ polymerization of acrylonitrile, styrene or preferably mixtures of styrene and acrylonitrile, for example in a weight ratio of from 90:10 to 10:90, preferably from 70:30
 20 to 30:70, expediently in the abovementioned polyetherpolyols, analogously to German patents 1111394, 1222669 (US 3304273, 3383351, 3523093), 1152536 (GB 1040452) and 1152537 (GB 987618), and polyetherpolyol dispersions which contain, as the disperse phase, usually in an amount of from 1 to 50, preferably from 2 to
 25 25, % by weight, for example polyureas, polyhydrazides, polyurethanes containing bound tertiary amino groups and/or melamine, and which are described, for example, in EP-B-011752 (US 4304708), US-A-4374209 and DE-A-3231497.

30 The polyetherpolyols can be used individually or in the form of mixtures.

In addition to the polyetherpolyols described, for example, polyetherpolyamines and/or further polyols selected from the
 35 group consisting of the polyesterpolyols, polythioetherpolyols, polyesteramides, hydroxyl-containing polyacetals and hydroxyl-containing aliphatic polycarbonates or mixtures of at least two of said polyols can also be used. The hydroxyl number of the polyhydroxy compounds is as a rule from 20 to 80,
 40 preferably from 28 to 56.

Suitable polyesterpolyols can be prepared, for example, from organic dicarboxylic acids of 2 to 12 carbon atoms, preferably aliphatic dicarboxylic acids of 4 to 6 carbon atoms, polyhydric
 45 alcohols, preferably diols, of 2 to 12, preferably 2 to 6 carbon atoms, by conventional processes. Usually, the organic polycarboxylic acids and/or polycarboxylic acid derivatives and

polyhydric alcohols are subjected to polycondensation, advantageously in a molar ratio of from 1:1 to 1.8, preferably from 1:1.05 to 1.2, in the absence of a catalyst or preferably in the presence of an esterification catalyst, expediently in an atmosphere comprising inert gas, e.g. nitrogen, carbon monoxide, helium, argon, etc., in the melt at from 150 to 250°C, preferably from 180 to 220°C, if required under reduced pressure, until the desired acid number is reached, which is advantageously less than 10, preferably less than 2. The polyesterpolyols obtained preferably have a functionality of from 2 to 4, in particular from 2 to 3, and a molecular weight of from 480 to 3000, in particular from 600 to 2000.

The flexible polyurethane foams can be prepared with or without the use of chain extenders and/or crosslinking agents, although as a rule these are not required. The chain extenders and/or crosslinking agents used are diols and/or triols having molecular weights of less than 400, preferably from 60 to 300. For example, aliphatic, cycloaliphatic and/or araliphatic diols of 2 to 14, preferably 4 to 10, carbon atoms, e.g. ethylene glycol, 1,3-propanediol, 1,10-decanediol, o-, m-, p-dihydroxycyclohexane, diethylene glycol, dipropylene glycol and preferably 1,4-butanediol, 1,6-hexanediol and bis(2-hydroxyethyl)hydroquinone, triols, such as 1,2,4- and 1,3,5-trihydroxycyclohexane, triethanolamine, diethanolamine, glycerol and trimethylolpropane, and low molecular weight hydroxyl-containing polyalkylene oxides based on ethylene oxide and/or 1,2-propylene oxide and the abovementioned diols and/or triols are suitable as initiator molecules.

If chain extenders, crosslinking agents or mixtures thereof are used for the preparation of the PUR foams, they are expediently used in an amount of up to 10% by weight, based on the weight of the polyol compounds.

The blowing agents (d) used may be the chlorofluoro carbons (CFCs) generally known from polyurethane chemistry and highly fluorinated and/or perfluorinated hydrocarbons. However, the use of these substances is greatly limited or has been completely discontinued for ecological reasons. In addition to chlorofluorohydrocarbons and fluorohydrocarbons, in particular aliphatic and/or cycloaliphatic hydrocarbons, in particular pentane and cyclopentane, or acetals, e.g. methylal, are possible alternative blowing agents. These physical blowing agents are usually added to the polyol component of the system. However, they may also be added to the isocyanate component or to both the polyol component and the isocyanate component as a combination.

It is also possible to use them together with highly fluorinated and/or perfluorinated hydrocarbons, in the form of an emulsion of the polyol component. If they are used, suitable emulsifiers are usually oligomeric acrylates which contain polyoxyalkylene and

5 fluoroalkane radicals bonded as side groups and have a fluorine content of from about 5 to 30% by weight. Such products are sufficiently well known from plastics chemistry, e.g.

EP-A-0351614. The amount of the blowing agent or of the blowing agent mixture used is from 1 to 25, preferably from 1 to 15, % by

10 weight, based in each case on the total weight of the components (b) to (d).

It is furthermore possible and usual to add water in an amount of from 0.5 to 15, preferably from 1 to 5, % by weight, based on the

15 total weight of the components (b) to (h), as a blowing agent to the polyol component. The addition of water can be effected in combination with the use of the other blowing agents described.

Catalysts (e) used for the preparation of the flexible

20 polyurethane foams are in particular compounds which greatly accelerate the reaction of the reactive hydrogen atoms, in particular of hydroxyl-containing compounds of components (b), (c) and (d), with the organic, unmodified or modified polyisocyanates (a). Organometallic compounds, preferably organic

25 tin compounds, such as tin(II) salts of organic carboxylic acids, e.g. tin(II) acetate, tin(II) octoate, tin(II) ethylhexanoate and tin(II) laurate, and the dialkyltin(IV) salts of organic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate, are

30 suitable. The organometallic compounds are used alone or, preferably, in combination with highly basic amines. Examples are amidines, such as 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine, tertiary amines, such as triethylamine, tributylamine, dimethylbenzylamine, N-methyl-, N-ethyl- and

35 N-cyclohexylmorpholine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylbutanediamine, N,N,N',N'-tetramethyl-1,6-hexanediamine, pentamethyldiethylenetriamine, tetramethyldiaminoethyl ether, bis(dimethylaminopropyl)urea, dimethylpiperazine,

40 1,2-dimethylimidazole, 1-azabicyclo[3.3.0]octane and preferably 1,4-diazabicyclo[2.2.2]octane, and aminoalkanol compounds, such as triethanolamine, triisopropanolamine, N-methyl- and N-ethyldiethanolamine and dimethylethanolamine. Other suitable catalysts are tris(dialkylaminoalkyl)-s-hexahydrotriazines, in

45 particular tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine, tetraalkylammonium hydroxides, such as tetramethylammonium hydroxide, alkali metal hydroxides, such as sodium hydroxide, and

alkali metal alcoholates, such as sodium methylate and potassium isopropylate, and alkali metal salts of long-chain fatty acids having 10 to 20 carbon atoms and, if desired, OH side groups. From 0.001 to 5, in particular from 0.05 to 2, % by weight, based on the weight of the components (b) to (h), of catalyst or catalyst combination are preferably used.

The stabilizers (f) used are in particular surfactants, i.e. compounds which serve to support the homogenization of the starting materials and may also be suitable for regulating the cell structure of the plastics. Examples are emulsifiers, such as sodium salts or castor oil sulfates or fatty acids and salts of fatty acids with amines, e.g. the salt of oleic acid with diethylamine, of stearic acid with diethanolamine and of ricinolic acid with diethanolamine, salts of sulfonic acids, for example alkali metal or ammonium salts of dodecylbenzene- or dinaphthylmethanedisulfonic acid and ricinoleic acid; foam stabilizers, such as siloxane/oxyalkylene copolymers and other organopolysiloxanes, oxyethylated alkylphenols, oxyethylated fatty alcohols, liquid paraffins, castor oil ester or ricinoleic esters, Turkey red oil and peanut oil, and cell regulators, such as paraffins, fatty alcohols and dimethylpolysiloxanes. The surfactants are usually used in amounts of from 0.01 to 5 parts by weight, based on 100 parts by weight of the components (b) to (h).

According to the invention, melamine in amounts greater than 25% by weight, based on the total weight of the components (b) to (h), is used as flameproofing agents (g). The particle size of the melamine is usually from 1 to 100 μm , preferably from 10 to 50 μm .

Further suitable flameproofing agents, which may be used in combination with melamine, are, for example, tricresyl phosphate, tris(2-chloroethyl) phosphate, tris(2-chloropropyl) phosphate, tetrakis(2-chloroethyl) ethylene diphosphate, dimethyl methanephosphonate, diethyl diethanolaminomethylphosphonate and commercial halogen-containing polyols having flameproofing properties. In addition to the abovementioned halogen-substituted phosphates, inorganic or organic flameproofing agents, such as red phosphorus, hydrated aluminum oxide, antimony trioxide, arsenic oxide, ammonium polyphosphate and calcium sulfate or expanded graphite or mixtures of these flameproofing agents and/or, if required, aromatic polyesters may also be used for flameproofing the flexible polyurethane foams. In general, it has proven expedient to use from 5 to 50, preferably from 5 to 25, parts by weight of said flameproofing agents for, in each case,

100 parts by weight of the components (b) to (h). The amount of melamine is at least 60, preferably from 70 to 90, % by weight, based on the total amount of flameproofing agents used.

5 If required, further assistants and/or additives (h) may be incorporated into the reaction mixture for the preparation of the novel flameproofed flexible polyurethane foams. Examples are fillers, dyes, pigments and hydrolysis stabilizers as well as fungistatic and bacteriostatic substances.

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Fillers, in particular fillers having a reinforcing effect, are to be understood as meaning the conventional organic and inorganic fillers, reinforcing agents, weighting agents, agents for improving the abrasion behavior in surface coatings, coating

15 agents, etc., known per se. Specific examples are inorganic fillers, such as silicate minerals, for example sheet silicates, such as antigorite, serpentine, hornblendes, amphiboles, chrysotile and talc, metal oxides, such as kaolin, aluminums, titanium oxides and iron oxides, metal salts, such as chalk,
 20 barite and inorganic pigments, such as cadmium sulfide and zinc sulfide, and glass etc. Kaolin (China clay), aluminum silicate and coprecipitates of barium sulfate and aluminum silicate, and natural and synthetic fibrous minerals, such as wollastonite, and metal fibers and in particular glass fibers of various lengths,
 25 which, if desired, may be sized, are preferably used. Examples of suitable organic fillers are carbon, rosin, cyclopentadienyl resins and graft polymers, and cellulose fibers and polyamide, polyacrylonitrile, polyurethane and polyester fibers based on aromatic and/or aliphatic dicarboxylic esters, and in particular
 30 carbon fibers. The inorganic and organic fillers may be used individually or as mixtures and are incorporated into the reaction mixture advantageously in amounts of from 0.5 to 50, preferably from 1 to 40, % by weight, based on the weight of the components (a) to (c), it being possible for the content of
 35 matts, nonwovens and woollen fabrics of natural and synthetic fibers to reach values of up to 80.

More detailed information on the abovementioned other conventional assistants and additives is to be found in the

40 technical literature, for example the monograph by J.H. Saunders and K.C. Frisch "High Polymers", Volume XVI, Polyurethanes, Parts 1 and 2, Interscience Publishers 1962 and 1964, or in the above-cited Kunststoffhandbuch, Polyurethane, Volume VII, Hanser Verlag Munich, Vienna, 1st to 3rd Editions.

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For the preparation of the novel foams, the organic and/or modified organic polyisocyanates (a), the polyetherol mixture (b) and, if required, further compounds (c) having hydrogen atoms reactive toward isocyanates, and further components (d) to (h),
5 are reacted in amounts such that the ratio of the number of equivalents of NCO groups of the polyisocyanates (a) to the sum of the reactive hydrogen atoms of the components (b) to (h) is from 0.70:1 to 1.25:1, preferably from 0.90:1 to 1.15:1.

10 Polyurethane foams according to the novel process are advantageously prepared by the one-shot process, for example with the aid of the high pressure or low pressure technique, in open or closed molds, for example metallic molds. The continuous application of the reaction mixture to suitable belt lines for
15 producing foam slabs is also usual.

It has proven particularly advantageous to employ the two-component process and to combine the components (b) to (h) into a polyol component, often also referred to as component A,
20 and to use, as the isocyanate component, often also referred to as component B, the organic and/or modified organic polyisocyanates (a), particularly preferably an NCO prepolymer or mixtures of these prepolymers and further polyisocyanates, and, if required, blowing agents (d).

25 The starting components are mixed at from 15 to 90°C, preferably from 20 to 60°C, in particular from 20 to 35°C and introduced into the open mold or, if desired, under superatmospheric pressure into the closed mold or, in the case of a continuous workstation,
30 applied to a belt which receives the reaction materials. Mixing can be carried out mechanically by means of a stirrer, by means of a stirring screw or by means of high-pressure mixing in a nozzle. The mold temperature is expediently from 20 to 110°C, preferably from 30 to 60°C, and in particular from 35 to 55°C.

35 The flexible polyurethane foams prepared by the novel process have a density of from 10 to 800, preferably from 30 to 100, in particular from 30 to 80, kg/m³. They are particularly suitable as upholstery for furniture and vehicle seats.

40 The examples mentioned illustrate the invention but without restricting it.

A flexible polyurethane foam based on the components mentioned in
45 Table 1 is foamed at a mold temperature of 50°C (KZ 95).

Table 1: Flameproofed flexible foams

		Example 1	Example 2	Example 3
5	Polyol (b1)	27.46	33.36	13.36
	Polyol (b2)	20	20	40
	Polyol (c)	2	5	5
	Melamine	35	35	35
	TCPP	8	4	4
10	Ultracarb	5		
	Lupragen® N 201	0.3	0.4	0.4
	Lupragen® N 206	0.1	0.1	0.1
	B 4113	0.24	0.24	0.24
	Water	1.9	1.9	1.9
15	Lupranat® MI	80	70	
	Lupranat® M20A	20	30	
	B 628			100
	Paper wad test	+	+	+
	Crib VII	+	n.d.	+

- 20 Polyol (b1) OH number 28 mg KOH/g, polyether alcohol based on propylene oxide and ethylene oxide, initiator glycerol, EO content 14%, primary OH groups 79% (BASF);
- 25 Polyol (b2) OH number 55 mg KOH/g, polyether alcohol based on propylene oxide and ethylene oxide, initiator glycerol, primary OH groups 46% (BASF);
- 25 Polyol (c) OH number 42 mg KOH/g, polyether alcohol based on propylene oxide and ethylene oxide (81%) (BASF);
- 30 Lupragen® N 201 amine catalyst (BASF);
- 30 Lupragen® N 206 amine catalyst (BASF);
- B 4113 silicone stabilizer (Goldschmidt)
- Lupranat® MI NCO content 33.6% by weight, mixture of diphenylmethane 4,4'- and 2,4'-diisocyanate isomers;
- 35 Lupranat® M20A NCO content 31.6% by weight, polyphenylenepolyurethane polyisocyanate;
- B 628 isocyanate prepolymer based on diphenylmethane diisocyanate, NCO content 26.9% by weight
- Lupragen® TCPP flameproofing agent (BASF);
- 40 Ultracarb flameproofing agent (Frank&Schulte GmbH)
- Paper wad test DIN 5510, Part 2
- Crib VII British Standard BS 5852

Claims

1. A process for the preparation of a flameproofed flexible polyurethane foam by reacting an organic polyisocyanate and/or a modified organic polyisocyanate (a) with a polyetherol mixture (b) and, if required, one or more further compounds (c) having one or more hydrogen atoms reactive toward isocyanates, in the presence of water and/or one or more other blowing agents (d), catalysts (e), stabilizers (f), flameproofing agents (g) and, if required, one or more further assistants and additives (h), wherein the polyetherol mixture (b) comprises
 - b1) at least one polyetherol which is at least difunctional, is based on propylene oxide and/or butylene oxide and ethylene oxide, the ethylene oxide content being less than 25% by weight based on the total amount of alkylene oxide used, has an OH number of from 20 to 80 mg KOH/g and contains more than 70% of primary OH groups, and
 - b2) at least one polyetherol which is based on propylene oxide and/or butylene oxide and ethylene oxide, has an OH number of more than 30 mg KOH/g and contains less than 70% of primary OH groups,and melamine, if desired as a mixture with one or more further flameproofing agents, is used as flameproofing agent (g).
2. A process as claimed in claim 1, wherein the weight ratio of (b1) to (b2) is greater than 0.3:1.
3. A process as claimed in claim 1 or 2, wherein melamine is used in an amount greater than 25% by weight, based on the total weight of the components (b) to (h).

4. A process as claimed in any of claims 1 to 3, wherein water is used in an amount of from 1 to 5% by weight, based on the total weight of the components (b) to (h).
- 5 5. A process as claimed in any of claims 1 to 4, wherein the organic and/or modified organic polyisocyanate (a) used is selected from tolylene diisocyanate, mixtures of diphenylmethane diisocyanate isomers, mixtures of diphenylmethane diisocyanate and polyphenylpolymethylene polyisocyanate or tolylene diisocyanate with
10 diphenylmethane diisocyanate and/or polyphenylpolymethylene polyisocyanate.
6. A process as claimed in any of claims 1 to 5, wherein the organic and/or modified organic polyisocyanate (a) used is a mixture of diphenylmethane diisocyanate isomers with at
15 least 10% by weight of diphenylmethane 2,4'-diisocyanate.
7. A process as claimed in any of claims 1 to 6, wherein the organic and/or modified organic polyisocyanate (a) used is an NCO-containing prepolymer formed from the reaction of the isocyanate(s) (a) with the polyetherol mixture (b) and, if required, the component(s) (c) and/or (d).
20
8. A process for the preparation of a flameproofed flexible polyurethane foam carried out substantially as hereinbefore described or exemplified in any of the foregoing Examples 1 to 3.
- 25 9. A flexible polyurethane foam, which is obtainable by a method claimed in any of claims 1 to 7.
10. The use of a flexible polyurethane foam as claimed in claim 9 as upholstery for furniture and vehicle seats.
11. A polyetherol mixture for use in the preparation of flameproofed flexible polyurethane foams, the mixture comprising
30

- 5 b1) at least one polyetherol which is at least difunctional, is based on propylene oxide and/or butylene oxide and ethylene oxide, the ethylene oxide content being less than 25% by weight based on the total amount of alkylene oxide used, has an OH number of from 20 to 80 mg KOH/g and contains more than 70% of primary OH groups, and
- 10 b2) at least one polyetherol which is based on propylene oxide and/or butylene oxide and ethylene oxide, has an OH number of more than 30 mg KOH/g and contains less than 70% of primary OH groups.



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Application No: GB 0122415.3
Claims searched: 1-10

Examiner: Dr Albert Mthupha
Date of search: 6 April 2002

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.T): C3R
Int Cl (Ed.7): C08G (18/48)
Other: ONLINE : EPODOC, JAPIO, WPI.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	US 5229427 A MILES, see column 6 line 37-column 7 line 2, Claims 1, 4.	1, 3, 4, 5, 9, 10.
Y	US 4143004 A BEROL KEMI, see Examples A, B, 1, 2, & 3.	1, 3, 4, 5, 9, 10.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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